Erosion of Graphite in Solid-Propellant Combustion Gases and Effects on Heat Transfer

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This paper presents the results of an analytical study and analysis of test data indicating that the erosion of graphite and graphite reinforced plastics in an aluminized solid-propellant rocket motor is primarily the result of a chemical reaction occurring at the surface. The extent of chemical erosion is dependent upon the nature of the reaction, rate limited or diffusion limited, and by the chemically active species occurring in the boundary layer. The effect of high-temperature chemical reactions on heat-transfer rates to the graphite surface has also been investigated and is presented in this paper. The primary constituents in the exhaust stream of an aluminized polybutadiene acrylic acid ammonium perchlorate propellant reacting with the graphite were found to be H_2O, CO_2, O_2, O, and OH. The reaction of these species with graphite is an endothermic reaction resulting in a substantial reduction in the heat-transfer rate to the surface. The chemical erosion of graphite has been expressed as simply a function of the reacting species, wall temperature, and enthalpy heat-transfer coefficient. The effects of chemical erosion of graphite on convective heating rates may be accounted for by the net heats of reaction involved or by the resulting effect on wall enthalpy.

Nomenclature

A/A^* = nozzle area ratio, dimensionless
B_r = frequency factor, lb/ft^2-sec-atm$^{1/2}$
C_H = enthalpy heat-transfer coefficient, lb/ft^2-sec
C_j = concentration of the j species, lb/lb$_{\text{gas}}$
C^* = propellant characteristic exhaust velocity, fps
D = diffusion coefficient, ft^2/sec
d_t = throat diameter, ft
E = activation energy, kcal/mole
ΔH_R = net heat of reaction, Btu/lb$_c$
ΔH_f = heat of formation of j species, Btu/lb$_j$
I_r = recovery enthalpy, Btu/lb
I_w = wall enthalpy, Btu/lb
I_{w_e} = effective-wall enthalpy, Btu/lb
I_{w_R} = wall enthalpy for equilibrium limited reaction, Btu/lb
K = atomic mass fraction, lb/lb$_{\text{mix}}$
k_r = reaction-rate constant, sec^{-1}
L_e = Lewis number, dimensionless
$\dot{m}$ = mass flow-erosion rate, lb/ft^2-sec
MW = molecular weight, lb/mole
P_c = motor-chamber pressure, psf
P_j = partial pressure of the j species, atm
P_r = Prandtl number, dimensionless
$\dot{q}$ = convective heat flux, Btu/ft^2-sec
$\Delta\dot{q}$ = increment of heat flux attributed to chemical reaction, Btu/ft^2-sec
r_c = throat radius of curvature, ft
R = universal-gas constant
St_0 = Stanton number without transpiration, dimensionless
St = Stanton number with transpiration, dimensionless
T = temperature, °R
u = velocity, fps
X_j = mole fraction of the j species, dimensionless
α = $\frac{1}{3}$ for $(MW)_g/(MW)_{iv} \leq 1$ and = $\frac{4}{5}$ for $(MW)_g/(MW)_{iv} > 1$
β = blowing rate = $\dot{m}/\rho_e u_e St_0$, dimensionless
η = transpiration effectiveness, dimensionless
μ = viscosity, lb/ft-sec
ρ = density, lb/ft^3
ν = stoichiometric coefficient, dimensionless
$\rho_e u_e$ = freestream mass flow rate, lb/ft^2-sec
ψ = dimensionless factor accounting for variation of viscosity and density across boundary layer[7]

Subscripts

c = pertaining to carbon
DL = diffusion limited
e = evaluated at boundary-layer edge
g = combustion products
iv = pertaining to injected vapors
j = jth chemical species
mix = propellant gas and condensable mixture
RL = rate limited
r = recovery value
s = pertaining to solid
t = total
v = pertaining to vapor
w = evaluated at wall conditions

Introduction

GRAPHITE and graphite reinforced plastics are important construction materials in solid-propellant rocket motors, and the behavior of these materials when subjected to the severe thermal environment is important in both ballistic performance and insulation evaluation.

For some time, the erosion of graphite has been attributed to mechanical, particulate, and chemical mechanisms. Work by the authors has indicated that graphite erosion is caused primarily by a chemical mechanism; the extent of the chemical erosion is dependent upon the nature of the reaction, rate limited or diffusion limited, and by the chemically active species occurring in the boundary layer.

The chemical erosion of graphite also has significant effects on heat-transfer rates to the surface of the material. With most of the present composite solid-propellant formulations using hydrocarbon binders with ammonium perchlorate oxidizer and aluminum, the reaction of graphite with the exhaust gases results in an endothermic reaction and reduction in heat-transfer rates to the graphite surface. Certain higher-

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energy propellants using different metal additives and oxidizers may react exothermically with the graphite, resulting in an increase in erosion and heat-transfer rates. The mechanism of this erosion and its effect on heat transfer are the subject of this paper.

Discussion

The establishment of the chemical mechanisms of graphite erosion was first obtained by analyzing the performance of graphite-throat inserts in 5-in.-center perforated motors ($\frac{7}{8}$-in. throat with a 3-sec burning time) using various propellant formulations. Even though the transient heating effects had a significant influence on the quantitative test results, the test data obtained from these 5-in. motors did provide a good qualitative analysis of the influence of various propellant combustion products on the erosion of graphite. The propellant formulations were altered by varying the amount of aluminum, oxidizer, and binder in the systems. If the erosion of graphite was primarily the result of a mechanical mechanism, particle impaction or shear, or a simple thermal degradation, the amount of erosion would be expected to increase in the more particle-laden streams (Al_2O_3) with the higher combustion temperatures. The data from these motors indicated that the erosion decreased with increase in aluminum content as shown in Fig. 1. From these data, it was postulated that the erosion of graphite was primarily the result of a chemical reaction occurring within the boundary layer.

A chemical equilibrium analysis[1] was conducted to determine the composition of the chemical species present in the exhaust products of each of the propellant formulations. Results of this analysis for three typical propellants are shown in Table 1. It was noted from this analysis that, of the major reactive constituents, the amount of water vapor HCl, and CO_2 along with Cl, Cl_2, OH, O, and O_2 decreased with increased aluminum content.

In order to determine whether the chlorine or oxygen-containing species were the primary reactants with carbon at high temperatures, an analytical chemical equilibrium composition analysis was made. In this analysis, it was necessary to consider the extra carbon being evolved from the reacting wall. This was done by using equations developed by Rindal.[2] The total amount of elemental carbon (K_c) available for chemical reaction at the heated surface was calculated from Rindal's approach using atomic mass fractions

Table 1 Chemical equilibrium gas composition[a] for example propellant formulations

Species	Type *A*	Type *B*	Type *C*
H	−1 354143	−1 449169	−1 464544
N	−5 540212	−5 716489	−5 694319
Cl	−1 112167	−2 921869	−2 545084
O	−3 636756	−3 412156	−3 148564
Al	−3 124734	−3 586312	−2 214835
C	−8 252383	−8 817793	−7 197677
AlO	−3 150282	−3 331664	−3 476617
AlCl	−2 413530	−1 116707	−1 274667
AlH	−4 319408	−3 157573	−3 630436
$AlCl_2$	−2 845877	−1 153159	−1 228033
$AlCl_3$	−4 650173	−4 778354	−4 728090
Al_2O	−3 106884	−3 780366	−2 450176
AlOCl	−4 406447	−4 570654	−4 519784
Al_2O_3 (liquid)	−1 829096	−1 955427	101003
C_2H_2	−9 370836	−8 223010	−7 182387
CO_2	−1 145442	−2 709751	−2 287888
Cl_2	−4 183157	−4 106354	−5 389153
CO	214301	223824	231238
HCN	−5 559414	−4 135464	−4 377644
HCl	127334	100301	−1 661149
H_2	268539	325460	375502
H_2O	141461	−1 809427	−1 365794
HClO	−3 112421	−3 139304	−3 152803
NH	−4 176176	−4 233798	−4 233893
N_2	−1 812529	−1 775172	−1 740305
NO	−3 602692	−3 344579	−3 124886
OH	−2 838136	−2 521026	−2 209270
O_2	−3 133869	−4 408264	−5 576681

[a] Values presented are mole fraction and are expressed in exponential form, i.e., −3 442527 is 0.442527 × 10^{-3}.

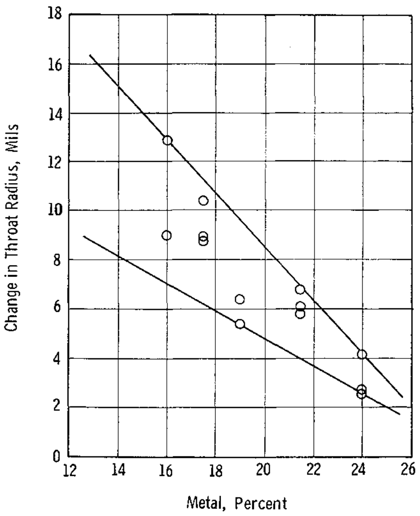

Fig. 1 **Effect of propellant composition on graphite-throat erosion.**

$$(K_{c,v})_w = \frac{(K_{c,v})_w + (\dot{m}/\rho_e u_e St_0) K_{c,s}}{1 + (\dot{m}/\rho_e u_e\, St_0)} \tag{1}$$

The ratio of the total atomic carbon at the wall to the boundary-layer edge can then be expressed as

$$\frac{(K_{c,v})_w}{(K_{c,v})_e} = \frac{1 + [K_{c,s}/(K_{c,v})_e](\dot{m}/\rho_e u_e\, St_0)}{1 + (\dot{m}/\rho_e u_e\, St_0)} = \frac{1 + [K_{c,s}/(K_{c,v})_e]\beta}{1 + \beta} \tag{2}$$

where

$$\beta = (\dot{m}/\rho_e u_e\, St_0) \tag{3}$$

The total available atomic carbon was used in a chemical equilibrium composition computer program[1] with a typical propellant formulation to determine the products formed when carbon reacts with the combustion gases. The carbon is oxidized while the chlorine reacts with the aluminum (Fig. 2). It also should be noted from Fig. 2 that the amount of CO_2 decreases and is small compared to the quantity of CO; therefore, H_2O, CO_2, OH, O, and O_2 were considered to be the primary reactants with graphite, and oxidation of the graphite results in the formation of CO.

The experimental erosion data from Fig. 1 were replotted as a function of the amount of the reacting species H_2O, CO_2, OH, O, and O_2 present in the system. The results shown in Fig. 3 tend to confirm the oxidation hypothesis.

Reaction-Rate Limited Erosion

For the rate limited solution, it can be shown that the erosion of graphite is governed by the half-order reaction based on a form of the Arrhenius equation and expressed as

$$\dot{m}_{RL} = k_r \Big(\sum_j P_j\Big)^{1/2} \tag{4}$$

where

$$k_r = B_r \exp(-E/RT_w) \tag{5}$$

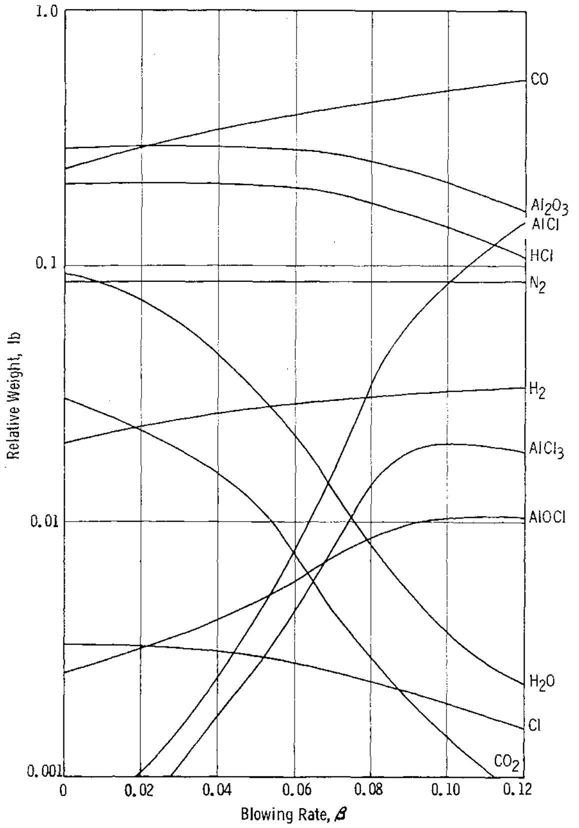

Fig. 2 Chemical equilibrium gas composition analysis.

and

$$\sum_j P_j = \left[\sum_j X_j \Big/ \left(1 - \sum_j X_j\right)\right] P_T \qquad (6)$$

Values of the activation energy (E), frequency factor (B_r), and the order of the reaction are not clearly defined. The mass erosion rate for a rate limited reaction becomes highly dependent upon the temperature, frequency factor (B_r), and the resulting reaction-rate constant (k_r). From the literature,[3] it was found that the frequency factor can vary by many orders of magnitude for various types of graphite. Reported values for the frequency factor vary from 6.73 × 10^8 lb/ft^2-sec-atm$^{1/2}$ for some commercial graphites to 1.28 × 10^4 lb/ft^2-sec-atm$^{1/2}$ for some pyrolytic graphites, and values of activation energy (E) vary from 32.8 kcal/mole to 47.5 kcal/mole.[4]

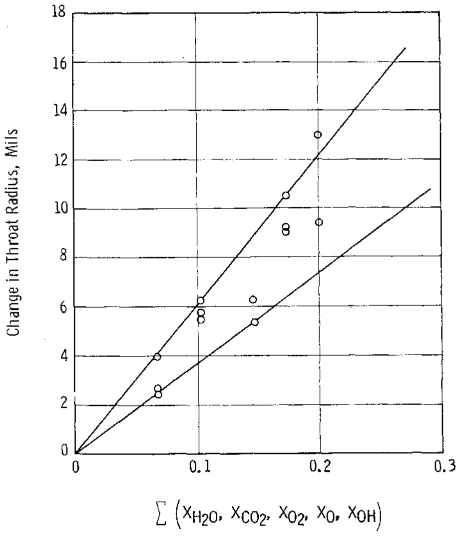

Fig. 3 Effect of combustion gas products on graphite-throat erosion.

Several values of the frequency factor (effective-collision frequency) were assumed to determine the effects on the predicted erosion rates. The results of this analysis are presented (Fig. 4), showing the rate limited mass erosion rate $\dot{m}_{RL}$ as a function of wall temperature. It can be noted from Fig. 4 that the mass erosion rate for a rate limited reaction is highly dependent upon the wall temperature and frequency factor. A low value for the frequency factor yielded good correlation with measured erosion rates at wall temperatures between 2500° and 2700°R (Fig. 5). A transient heating analysis was conducted to determine the transient temperature response of the graphite surface; the average wall temperatures were calculated to be between these two values (2500°–2700°R). The motors used in these tests were the same subscale motors mentioned previously with very high-density graphite-throat inserts.

An erosion analysis of larger nozzles (D_t = 7 in.) fired on motors with longer burn times (approximately 60 sec) was also conducted. The graphite used in these motors was the same as in the smaller motors, but the predicted erosion using the same kinetic constants was much lower than the measured values. In the larger motors where transient effects were negligible and the graphite surface was near steady-state temperature (5500°R), the measured erosion rates were nearly five times greater than predicted. An explanation for these large differences could be from the kinetic constants used for the predictions. An error in the kinetic constants would not have as much influence on the predicted results for motors with short burn times, because no erosion occurs for a significant portion of the firing. The kinetic constants for the high-density graphite tested were not available, so that values very close to those of pyrolytic graphite were assumed. Measured erosion rates from some pyrolytic graphite materials have shown erosion rates of the magnitude predicted. The rate limited method of predicting erosion would be satisfactory if the correct critical constants are known for the graphite material being analyzed.

Chemical Equilibrium Erosion Analysis

Since the Arrhenius equation is limited by the data available for the frequency factor (B_r), as well as the activation energy (E) for the graphite reaction, a technique suggested by Rindal[2] was used to obtain a limiting erosion rate based

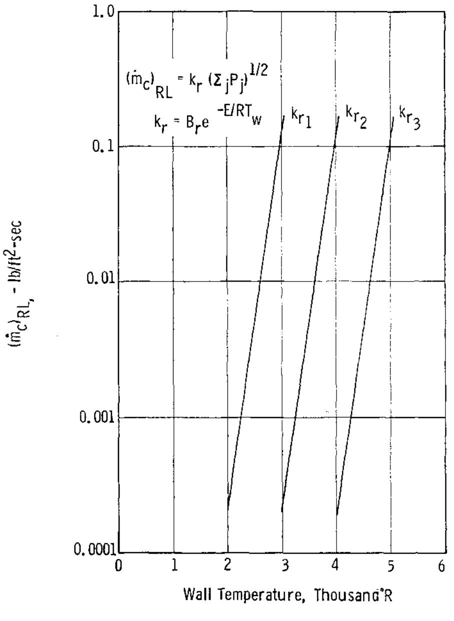

Fig. 4 Effect of wall temperature and reaction-rate constant on the chemical erosion of graphite.

on chemical equilibrium considerations. The chemical equilibrium approach results in the maximum erosion rate possible, because the reaction-rate constants are considered to be infinite. At the boundary-layer/wall interface, the residence time is sufficiently long to allow chemical equilibrium to be approached. The chemical equilibrium analysis represents a more accurate approach to the reaction-rate limit in that all chemical reactions can be considered. This approach also has an advantage over the reaction rate in that the thermochemical equilibrium equations are developed for the computer. Thermochemical data are available, whereas the reaction-rate constants are not.

The chemical equilibrium technique incorporates the same procedure presented previously in Eq. (2) to evaluate the additional atomic mass fraction of carbon that would be present in the chemical constituents formed from the propellant combustion gases and the eroding graphite. An equilibrium chemical composition is then obtained for the given erosion rate as a function of temperature. The temperature where all condensed carbon disappears represents the wall temperature that would exist at the given blowing rate. The mole fraction of condensed carbon for an example propellant is presented in Fig. 6 for several blowing rates. It can be seen that, as the blowing rate is increased, the equilibrium wall temperature also increases. A replot of the blowing rate and temperature intercepts (Fig. 7) illustrates the normalized erosion rate temperature dependence. The solid line in Fig. 7 represents the results of a thermochemical equilibrium analysis considering all possible reactions, and the dotted line represents the effect on the blowing rate (β) neglecting any carbon-hydrogen reactions. It should be noted that the erosion parameter (β) becomes relatively constant if the hydrogen reactions are neglected at the wall temperatures that are expected in a rocket motor (T_w >3500°R). This constant line would indicate that the erosion mechanism may become limited by the diffusion of the selected reactive species (oxidizing gases) to the graphite wall. If the carbon-hydrogen reactions are significant, the erosion rate would continue to increase significantly as the wall temperature increases.

Diffusion Controlled Erosion

An analytical approach developed by Lafazan[5] was devised for predicting erosion for diffusion controlled chemical reactions. The mass erosion rate $\dot{m}_{DL}$ of graphite for a diffusion limited reaction is dependent upon the rate of diffusion of the chemically reactive species through the boundary layer to the surface. The mass rate of diffusion of a reactive species through the boundary layer to the wall is given by the diffusion equation

$$(m_j)_w = \rho u C_j - \rho D_j(\partial C_j/\partial Y) \tag{7}$$

For conditions at the wall, considering infinite reaction rates, the concentration of the reactive species is zero

$$(\dot{m}_j)_w = -\rho D_j\,(\partial C_j/\partial Y)_w \tag{8}$$

or

$$(\dot{m}_j)_w = (-\mu/P_r)(\partial C_j/\partial Y)_w \tag{9}$$

The mass rate of chemical ablation of carbon at the wall is related to the mass rate of diffusion of the reactive species by the number of moles of the reactants present:

$$(\dot{m}_c)_w = [(MW)_c/(MW)_j](\dot{m}_j)_w \tag{10}$$

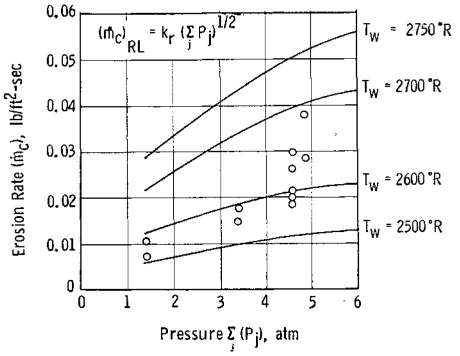

Fig. 5 Reaction-rate controlled erosion of graphite for various propellant formulations.

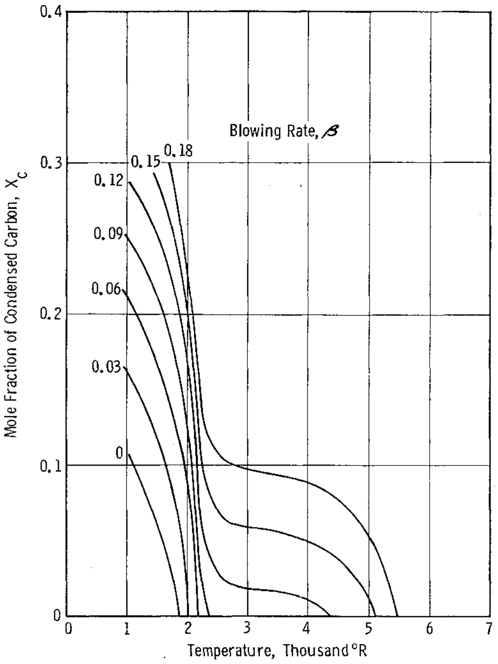

Fig. 6 Mole fraction of condensed carbon in chemical equilibrium.

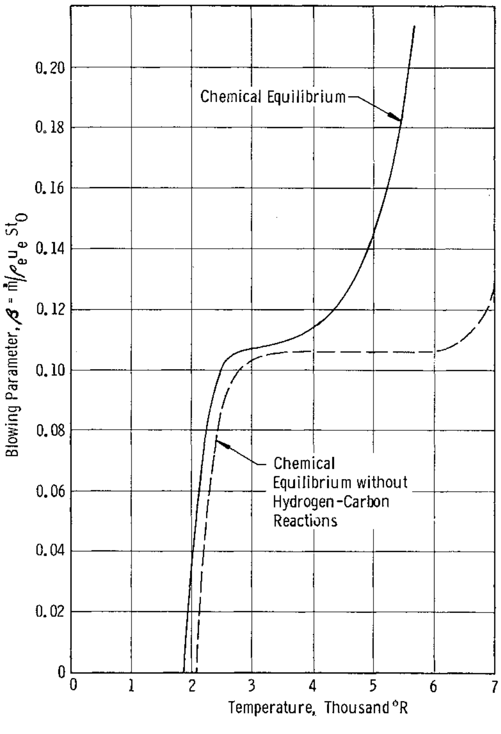

Fig. 7 Graphite erosion blowing coefficient chemical equilibrium limit.

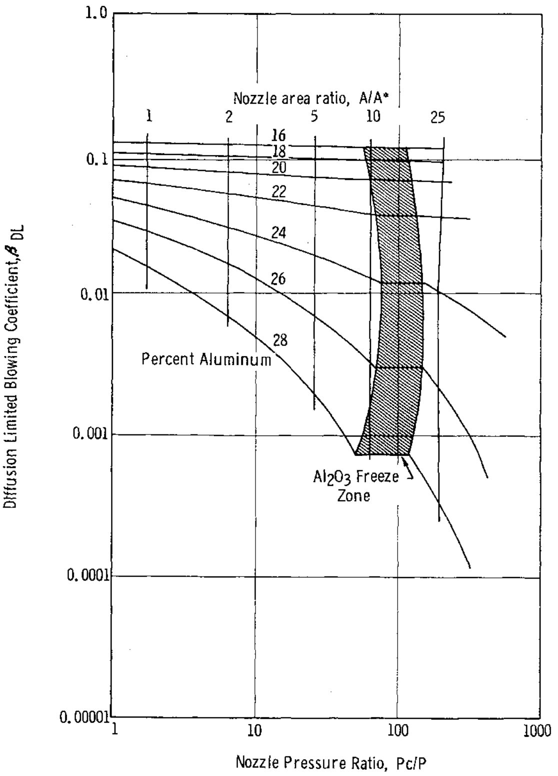

Fig. 8 Effect of metal additive on diffusion limited blowing parameter.

Assuming that the Lewis and Prandtl numbers are unity, then

$$(\partial C_i/\partial Y)_w = (\rho_e u_e\, St/\mu)C_{i,e} \qquad (11)$$

where St is the Stanton number with mass injection into the boundary layer. Lafazan defines the ratio of Stanton numbers with and without mass injection as

$$St/St_0 = 1 - \eta\beta_{DL} \qquad (12)$$

where η is the transpiration effectiveness, and β_{DL} is the blowing rate.

Combining Eqs. (9–12) and including all reactions results in[5]

$$(\dot{m}_c)_w/\rho_e u_e\, St_0 = \beta_{DL} \qquad (13)$$

where

$$\beta_{DL} = \frac{\Sigma(\nu_c MW_c/\nu_i MW_i)C_{i,e}}{1 + \eta\Sigma(\nu_c MW_c/\nu_i MW_i)C_{i,e}} \qquad (14)$$

Hidalgo[6] arrives at an expression similar to Eq. (12) for determining the effects of mass injection on the boundary layer and, consequently, on ablation rates. Using Hidalgo's analysis, the transpiration effectiveness (η) can be written as

$$\eta = \tfrac{1}{5}(Pr)^{2/3}(MW_g/MW_w)^{\alpha} \qquad (15)$$

Measured graphite erosion rates are in the order of less than 0.1 lb/ft²-sec, and the molecular weight of the injected CO and H_2 vapors is around 15; therefore, the effect of transpiration on the Stanton number, as well as the blowing parameter (β_{DL}), may be neglected. The mass erosion rate of graphite may then be expressed as

$$\beta_{DL} = \frac{(\dot{m})_{DL}}{\rho_e u_e\, St_0} = \Sigma\,\frac{\nu_c(MW)_c}{\nu_i(MW)_i}\,C_{i,e} \qquad (16)$$

The concentration ($C_{i,e}$) for each reactive species may be determined from

$$C_{i,e} = \frac{(MW)_i}{(MW)_g(1 - X_{Al_2O_3}) - X_{Al_2O_3}\,MW_{Al_2O_3}}\,(X_{i,e}) \qquad (17)$$

This results in the following expression for β_{DL}:

$$\beta_{DL} = \frac{\dot{m}_{DL}}{\rho_e u_e\, St_0} =$$

$$\frac{(MW)_c}{(MW)_g(1 - X_{Al_2O_3}) - X_{Al_2O_3}(MW)_{Al_2O_3}}\,\Sigma\,\frac{\nu_c}{\nu_i}\,X_i \qquad (18)$$

The product of the mass flow rate at the edge of the boundary and the Stanton number are substituted by the enthalpy heat-transfer coefficient (C_H), and Eq. (18) may be written as

$$\dot{m}_{DL} = C_H\beta_{DL} \qquad (19)$$

The blowing parameter (β_{DL}) is calculated from the assumed chemical equations expressing the oxidation of graphite by H_2O, CO_2, O_2, O and OH to CO

$$H_2O + C \rightarrow H_2 + CO$$

$$CO_2 + C \rightarrow 2CO$$

$$O_2 + 2C \rightarrow 2CO$$

$$O + C \rightarrow CO$$

$$2OH + 2C \rightarrow H_2 + 2CO$$

The preceding stoichiometric equations result in the following expression for β_{DL}:

$$\beta_{DL} = \frac{(MW)_c}{(MW)_g(1 - X_{Al_2O_3}) - X_{Al_2O_3}(MW)_{Al_2O_3}}\,(X_{H_2O} + X_{CO_2} + 2X_{O_2} + X_O + X_{OH}) \qquad (20)$$

Values of β_{DL} for several propellant formulations were obtained from the chemical equilibrium composition of the solid-propellant combustion products (Fig. 8). This figure also indicates the effect that varying percentages of metal have on the diffusion limit blowing coefficient.

The diffusion limited blowing coefficient is presented in Fig. 9 for the same propellant used in Fig. 7 for calculating the chemical equilibrium blowing parameter. It should be noted that the diffusion limit coincides with the chemical equilibrium limit neglecting any carbon-hydrogen reactions

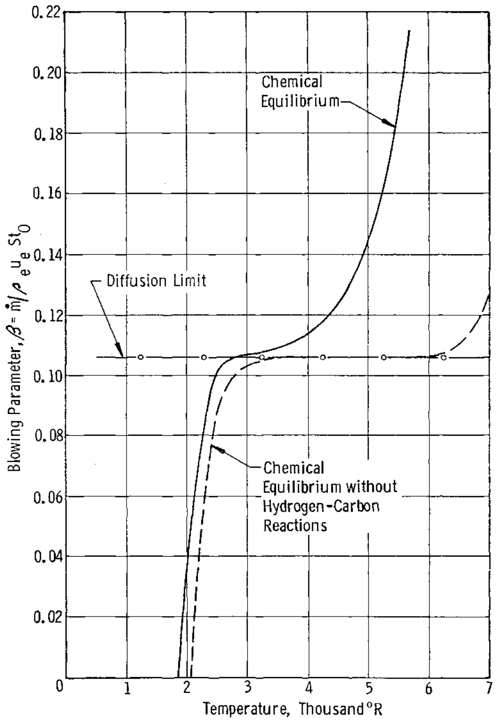

Fig. 9 Graphite erosion blowing coefficient chemical equilibrium and diffusion limit.

at wall temperatures expected in a rocket nozzle ($T_w >$ 3500°R).

The predicted graphite erosion rates based on the diffusion limit technique, Eq. (19), compared with measured erosion data from nine different propellant formulations with blowing rates (β_{DL}) ranging from 0.0237 to 0.131 are shown in Fig. 10. The presentation of the experimental data in this form required the evaluation of a convective heat-transfer coefficient. This was done using Bartz's simplified equation[7]

$$C_H = \frac{0.026}{d_t^{0.2}(A/A^*)^{0.9}} \left(\frac{\mu^{0.2}}{P_r^{0.6}}\right) \left(\frac{P_{cg}}{C^*}\right)^{0.8} \left(\frac{d_t}{r_c}\right)^{0.1} \psi \qquad (21)$$

The measured erosion data presented in Fig. 10 were obtained from motors with throat diameters ranging from 7 in. to 38 in., and burning times between 60 and 120 sec. These motors were sufficiently large, and the nozzles were flightweight or near flightweight design, such that the heat sink and transient heating period had negligible effects on the test results. It should also be noted from Fig. 10 that some of the erosion data were obtained from carbon reinforced plastics (carbon cloth phenolic and graphite cloth phenolic); the diffusion limited technique for predicting erosion appears to be equally satisfactory with graphite or graphite reinforced phenolics.

Effect of Erosion on Heat Transfer

The previous sections outline techniques whereby the erosion of graphite, as a function of wall temperature, can be evaluated analytically. This erosion also has a significant effect on the analytical evaluation of convective heat transfer. Since the erosion of graphite involves chemical reaction at the wall, the present analytical techniques must be modified to include the endothermic or exothermic reactions that occur.

Presently, the convective heating is evaluated using the following equation:

$$\dot{q}_{\text{conv}} = C_H(St/St_0)(I_r - I_w) \qquad (22)$$

where I_w is the wall enthalpy based on a nonreacting wall.

The convective heat-transfer equation may be corrected to account for the chemical reaction using the following methods. The first is to evaluate the wall-enthalpy/temperature relationship accounting for equilibrium limited chemical reactions. The second method is to add a separate term to the energy equation to account for the heat of reaction (diffusion limited reaction).

If chemical equilibrium is assumed at the wall-gas interface, the wall-enthalpy/temperature relationship may be evaluated; this was done for a typical propellant (Fig. 11). The wall enthalpy was evaluated at the appropriate blowing rate that corresponds to the wall temperature. Also included in Fig. 11 is the wall-enthalpy/temperature relationship assuming no reaction at the wall. As expected, the chemical reaction has a significant effect on the wall enthalpy.

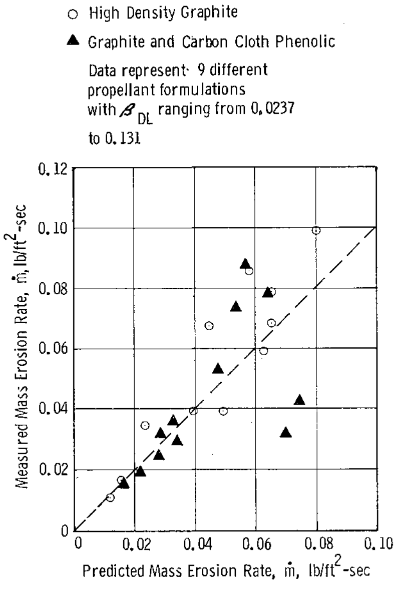

Fig. 10 Comparison of experimental and theoretical erosion rates.

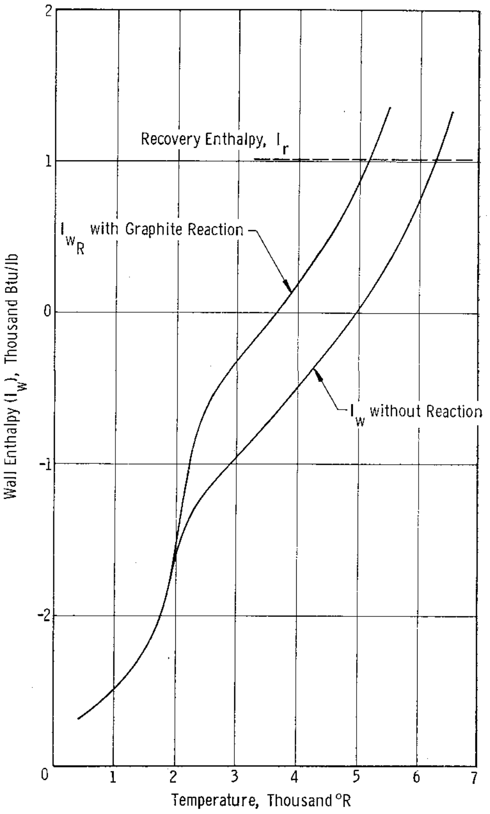

Fig. 11 Wall-enthalpy/temperature relationship.

In the diffusion limited region, an additional technique for correcting the energy equation is to evaluate the heat release or energy absorption from the predominate chemical reactions at the surface; this can be done by use of the following equation:

$$\dot{q}_{DL} = C_H(St/St_0)(I_r - I_w) - \dot{m}_{DL}\Delta H_R \qquad (23)$$

where

$$\dot{m}_{DL}\Delta H_R = \Delta\dot{q}_{DL} = \text{the increment of heat flux due to diffusion limited chemical reaction} \qquad (24)$$

As mentioned previously, the significant species reacting with carbon can be described by the following chemical equations:

$$H_2O + C \rightarrow H_2 + CO$$

$$CO_2 + C \rightarrow 2CO$$

$$2OH + 2C \rightarrow H_2 + 2CO$$

$$O_2 + 2C \rightarrow 2CO$$

$$O + C \rightarrow CO$$

Summarizing the preceding chemical equations and considering only the mole fractions of the reacting species results in the following equivalent stoichiometric equation:

$$X_{H_2O}H_2O + X_{CO_2}CO_2 + X_{O_2}O_2 + X_OO + X_{OH}OH + (X_{H_2O} + X_{CO_2} + 2X_{O_2} + X_O + X_{OH})C \rightarrow (X_{H_2O} + X_{OH}/2)H_2 + (X_{H_2O} + 2X_{CO_2} + 2X_{O_2} + X_O + X_{OH})CO$$

The net heat of reaction may be obtained easily from the previous stoichiometric equation and expressed as

$$\left.\begin{aligned}\Delta H_R = {} & [1/(MW)_c]\,\{[(X_{H_2O} + X_{OH}/2)(\Delta H_f)_{H_2} + \\ & (X_{H_2O} + 2X_{CO_2} + 2X_{O_2} + X_{OH} + X_O)(\Delta H_f)_{CO}] - \\ & [X_{H_2O}(\Delta H_f)_{H_2O} + X_{CO_2}(\Delta H_f)_{CO_2} + X_{O_2}(\Delta H_f)_{O_2} + \\ & X_{OH}(\Delta H_f)_{OH} + X_O(\Delta H_f)_O + (X_{H_2O} + X_{CO_2} + \\ & 2X_{O_2} + X_{OH} + X_O)(\Delta H_f)_C]\} \times \\ & [X_{H_2O} + X_{CO_2} + 2X_{O_2} + X_{OH} + X_O]^{-1}\end{aligned}\right\} \quad (25)$$

At the reference state (298°K), the heat of formation of all of the elements is considered to be equal to zero; Eq. (25) may be simplified to

$$\Delta H_R = \frac{1}{(MW)_c} \times \left\{\left[\frac{(X_{H_2O} + 2X_{CO_2} + 2X_{O_2} + X_{OH} + X_O)(\Delta H_f)_{CO}}{(X_{H_2O} + X_{CO_2} + 2X_{O_2} + X_{OH} + X_O)}\right] - \left[\frac{X_{H_2O}(\Delta H_f)_{H_2O} + X_{CO_2}(\Delta H_f)_{CO_2} + X_{OH}(\Delta H_f)_{OH} + X_O(\Delta H_f)_O}{(X_{H_2O} + X_{CO_2} + 2X_{O_2} + X_{OH} + X_O)}\right]\right\} \quad (26)$$

Values for the graphite heat of reaction with several propellants were evaluated and are included in Fig. 12. The heats of reaction were evaluated at 4500°R instead of the normal reference state (298°K), since this more closely approximates the average reaction temperature; consequently Eq. (25) was used.

The energy equation may also be corrected through the heat-transfer driving potential (enthalpy difference) by evaluating an effective-wall enthalpy (I_{w_e}) accounting for the oxidation reaction at the graphite surface. The convective heating rate then may be expressed by the following equation:

$$\dot{q}_{\text{conv}} = C_H(St/St_0)(I_r - I_{w_e}) \quad (27)$$

The effective-wall enthalpy (I_{w_e}) may be calculated easily by combining the preceding equation with Eq. (23)

$$C_H(St/St_0)(I_r - I_w) - \dot{m}_{DL}\Delta H_R = C_H(St/St_0)(I_r - I_{w_e}) \quad (28)$$

Substituting Eq. (19) for $\dot{m}_{DL}$ and simplifying results in the following expression for I_{w_e}

$$I_{w_e} = I_w + \beta_{DL}\Delta H_R \quad (29)$$

Values of (I_{w_e}) for a given propellant are presented in Fig. 13 and are compared to that previously obtained with a nonreacting wall (I_w) and to that assuming complete chemical equilibrium (I_{w_R}) accounting for all possible chemical reactions. It should be noted from Fig. 13 that the effective-wall enthalpy based on chemical equilibrium without carbon-hydrogen reactions is in good agreement with that calculated from Eq. (29) based on diffusion controlled erosion.

Conclusions

The erosion of graphite in a solid-propellant rocket motor is primarily a result of a chemical reaction between the graphite wall and the reactive species of the propellant combustion products. The chemical reaction is a rate controlled reaction during the period when the graphite is being transiently heated. If the kinetic constants are known, the erosion can be calculated by the Arrhenius reaction-rate equation. Since the reaction-rate constants exhibit large variations with different grades of graphite and in many cases are unavailable, the erosion can be more accurately predicted by assuming chemical equilibrium. The chemical equilibrium technique yields good results with present propellants if hydrogen-carbon reactions are neglected. The hydrogen-carbon reactions do not appear to be significant with present propellants. The erosion rate of graphite and graphite reinforced plastics becomes limited by diffusion of the oxidizing gases (H_2O, CO_2, O_2, O, and OH) at wall temperatures exceeding 3500° R. The diffusion limit approach can be used for predicting erosion of graphite and graphite reinforced plastics where transient effects are not significant.

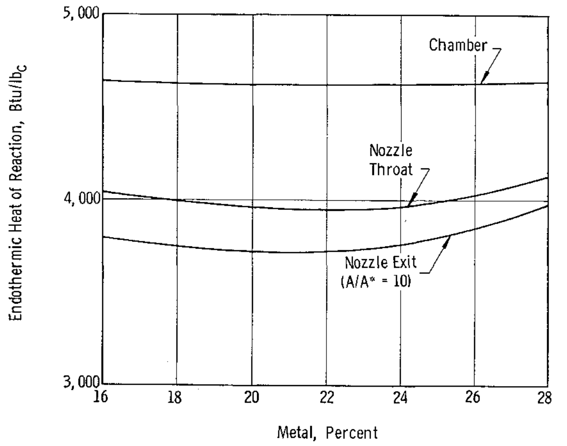

Fig. 12 Effect of propellant formulation on graphite heat of reaction.

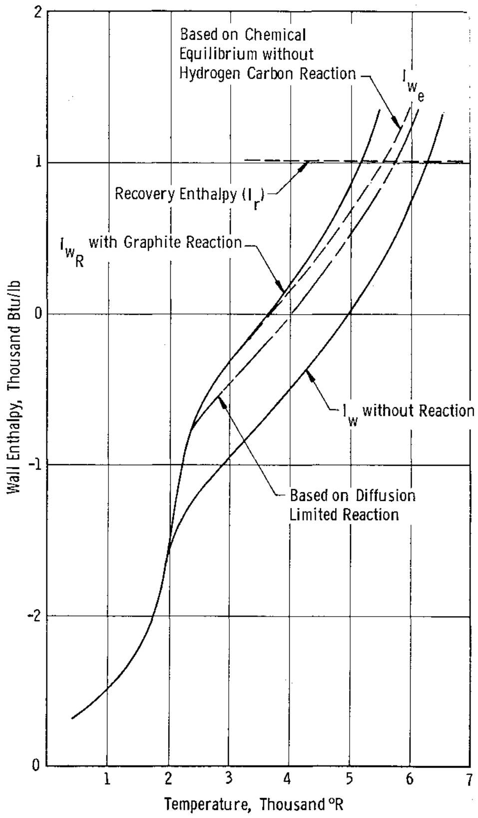

Fig. 13 Wall-enthalpy/temperature relationship.

The effect of chemical erosion on heat-transfer rates can be derived from the net heat of reaction involved and the resulting effect on wall enthalpy. The convective heating rate can be evaluated using the effective wall-enthalpy/temperature relationship, or the convective heat-transfer rate can be modified to account for the loss or absorption of energy associated with the chemical reaction occurring within the boundary layer.

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Linear Pyrolysis Rate Measurements of Propellant Constituents

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This paper discusses the construction and use of a device to measure linear pyrolysis rates of solid-propellant constituents. The device employs a radiantly heated porous plate. Propellant samples are pressed against the plate, and the pyrolysis rates corresponding to different interface temperatures are measured. The use of a porous plate represents a new approach, which seeks to avoid the problem associated with the obstruction of flow of pyrolysis products that occurs if a solid plate is used. This obstruction results in a gas film between the plate and the sample and, therefore, causes uncertainty in the evaluation of the sample surface temperature. Data for the linear pyrolysis of ammonium chloride and ammonium perchlorate have been obtained with this new device. Although subject to rather poor reproducibility, these data compare favorably with the existing data for these materials obtained with the original hot-plate technique. The data also are compared with similar data for propellant mixtures. In addition, a comparison of these experimental results with vapor-pressure data has allowed estimation of the surface accommodation coefficients. These were found to be of the order of 10^{-2} and 10^{-3}, respectively, for ammonium perchlorate and ammonium chloride.

Introduction

THE initial step in the chain of events occurring during propellant combustion is the conversion of the solid constituents to reactive gases. The description of this step is of prime importance in any theory that attempts to describe the over-all combustion process, since it represents the boundary condition that couples the conservation equations that are written normally for the solid and gaseous phases. Most theorists follow the idea proposed by Daniels[1] that surface gasification can be described as a monomolecular reaction, and that this step controls the over-all burning rate. Thus, the regression rate may be expressed in kinetic terms as

$$r = B \exp(-E/RT_s) \tag{1}$$

where r is the steady-state regression rate, B is the pre-exponential constant, which depends upon the kinetic frequency factor and the surface concentration of the decomposing molecules, E is the activation energy, R is the gas constant, and T_s is the surface temperature. Penner[2] has pointed out that, as long as a first-order gasification process occurs, the preceding equation remains valid independently of the interplay of surface and gas-phase reactions.

Shultz[3, 7] and Dekker[7] extended this line of reasoning to the burning of composite solids, suggesting that gasification of the oxidizer and binder proceed independently, both following a regression rate law of the form of Eq. (1), but each with a different activation energy and pre-exponential factor. As a consequence, the surface temperatures of the oxidizer and fuel must be different if both regress at the same mean rate. This reasoning is the basis for their "two-temperature" theory.

In more recent years, the concept of a surface gasification reaction, described mathematically by an equation of the form of Eq. (1), has been employed in theories for nonsteady-state combustion (e.g., Refs. 4 and 5). The objective of these theories has been the prediction of nonsteady combustion behavior based on a knowledge of more easily measured steady-state burning-rate parameters. In these theories, the surface gasification parameters strongly influence the predicted behavior. Therefore, experimental evaluation of these parameters is of practical interest.

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